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Adherent diamond-like carbon coatings on metals via plasma source ion implantation

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Abstract

Various techniques are currently used to produce diamond-like carbon (DLC) coatings on various materials. Many of these techniques use metallic interlayers, such as Ti or Si, to improve the adhesion of a DLC coating to a ferrous substrate. An alternative processing route would be to use plasma source ion implantation (PSII) to create a carbon composition gradient in the surface of the ferrous material to serve as the interface for a DLC coating. The need for interlayer deposition is eliminated by using a such a graded interface. A PSII approach has been used to form adherent DLC coatings on magnesium, aluminum, silicon, titanium, chromium, brass, nickel and tungsten. A PSII process tailored to create a graded interface allows deposition of adherent DLC coatings even on metals that exhibit a positive heat of formation with carbon, such as magnesium, iron, brass and nickel. © 1997 Elsevier Science S.A.

Keywords: Diamond-like carbon; Metals; Plasma source ion implantation; Adherence

1. Introduction

Diamond-like carbon (DLC) coatings are of technological interest for enhancing wear resistance [1,2] and corrosion resistance [3,4] of metals. Sputter cleaning of the surface [5,6] and interlayer deposition are two major surface preparation methods used to improve the adhesion of DLC coatings to metals. Interlayers, such as Si [7], Ti [8,9], TiC [8,10], TiN [8], TiCN [8], Mo [11] and Cu/Cr [12] are chosen for their ability to form strong bonds to the substrate and also to the DLC coating. As applications for DLC coating technologies expand to require coating of larger areas with more complex surface geometries of a wide range of metals, more versatile and universally applicable processing methods need to be developed [13,14]. This work details an effort to use methane (CH_4) and plasma source ion implantation (PSII) to produce an interface, graded in carbon composition, to improve the adherence of DLC coatings to a wide range of metals.

2. Experimental

Coupons of Mg alloy AM60, 99.999% Al and Al alloy A390, Si, Ti, Ti–6Al–4V, electrodeposited hard Cr (>2 μm) on 304 stainless steel, steel 1018, steel A36, steel 4340, stainless steels 303 and 304, tool steel M2, Ni, brass (Cu–Zn), Cu, WC (Co) and W were used to test the adhesion of DLC on a wide range of metals. Both polished (mirror finish) and unpolished coupons were used for each material, except for A390, Ti, 304, brass and Cu for which only unpolished coupons were included. Portions of the polished coupons were masked so that a surface profilometer could be used to measure the DLC coating thickness.

The ion implantation and DLC deposition experiments were conducted using the Los Alamos PSII facility [15] and the experimental conditions are shown in Table 1. The first sputter cleaning step is to remove metal oxides and other surface contaminants that could interfere with subsequent steps. A carbon composition gradient, needed to enhance the adhesion of the DLC coating, is produced by the carbon implantation step. During carbon implantation, neutral radicals from the methane plasma can deposit on the metal surface. This carbon coating is generally graphitic and not strongly adherent to the metal. The graphitic layer can reduce the adherence of DLC, so it is removed by the second sputter cleaning step. The experiments are concluded with DLC deposition. The main difference between Experiments I and III is the increased implantation bias which, by virtue of the higher ion range, gives a thicker

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Table 1
PSII processing parameters for each experiment

PSII processing steps	Experiment I $A=3$ m^2	Experiment II $A=0.26$ m^2	Experiment III $A=0.26$ m^2
Sputter cleaning (Ar)	$P=1.3$ Pa $V=2$ kV $\tau=20$ µs $f=4$ kHz $T=2.25$ h	$P=1.3$ Pa $V=2$ kV $\tau=30$ µs $f=5$ kHz $T=2.5$ h	$P=1.3$ Pa $V=2$ kV $\tau=30$ µs $f=5$ kHz $T=2.2$ h
Carbon implantation (CH_4)	$P=0.04$ Pa $V=20$ kV $\tau=20$ µs $f=700$ Hz $T=4.75$ h	None	$P=0.07$ Pa $V=50$ kV $\tau=20$ µs $f=2$ kHz $T=1.2$ h
Sputter cleaning (Ar)	Same as above $T=8$ min	None	Same as above $T=10$ min
DLC deposition (C_2H_2)	$P=0.07$ Pa $V=1.5$ kV $\tau=20$ µs $f=4$ kHz $T=48.5$ h $t=6.8$ µm	$P=0.05$ Pa $V=1.5$ kV $\tau=30$ µs $f=5$ kHz $T=3.5$ h $t=0.5$ µm	$P=0.04$ Pa $V=1.5$ kV $\tau=30$ µs $f=5$ kHz $T=3.5$ h $t=0.3$ µm

The parameters listed are working gas pressure (P), pulsed bias magnitude (V), pulse width (τ), pulse frequency (f), duration of the step (T), processed area (A) and DLC coating thickness (t).

graded interface. Experiment II did not include the carbon implantation step or the second sputter cleaning step.

Ion beam analysis [16], nanoindentation, and adhesion tests were performed to characterize the composition, hardness and adhesion strength of each coating. Nanoindentation measurements were accomplished using a Nanoindenter® II and the continuous stiffness mode. The adhesion strength of the DLC coatings was measured in tension using the Sebastian® II stud pull test.

3. Results and discussion

The deposition conditions of all experiments produced a DLC coating consisting of 70% carbon and 30% hydrogen and a hardness of ~20 GPa. The thickness of each coating is included in Table 1.

Table 2 contains a listing of the metals with both adherent and non-adherent DLC coatings for each experiment. The Ti sample in Experiment I was unpolished. It is believed that the sputter-cleaning and 20 kV PSII steps were insufficient to clean the machined surface and produce a graded interface extending into the bulk metal. Experiments II and III show that carbon implantation allows a DLC coating to adhere to brass and Ni. The DLC coating on A36 did not adhere when including a carbon implantation step, but the coating did adhere when the implantation step was omitted. It is believed that the A36 coupons were not in good thermal contact with the stage and the implantation step resulted in sample heating that interfered with DLC adhesion. Rutherford backscattering spectroscopy (RBS) analysis of the DLC coated tungsten samples (Fig. 1) shows the differences between the W spectra for Experiments II and III. First, the W-edge at channel 705 is shifted to the left for the DLC coated samples. The DLC coatings are of different thickness, so the W spectra are shifted different amounts. The RBS spectra for the carbon implanted and DLC coated W exhibit a region (channel 595–620) with a reduced yield. The reduced yield indicates an interface of graded C composition, ~50 nm thick, between the bulk W metal and the DLC coating. A similar reduction in yield is not observed for the DLC coated W that was not C implanted. The results show that PSII biases of 20–50 kV are sufficient to produce a graded interface between DLC and metals without the use of interlayers. Note that DLC adhesion is achieved even for metals, such as Mg, Fe and Ni, for which carbides are not thermodynamically favored [17,18].

The results of the adhesion tests are shown in Fig. 2. The adhesion of the epoxy to Al is included as an estimate of the strength of the epoxy. The adhesion of DLC to W and Mg are improved, but the result is less clear for M2. A more informative comparison is shown

Table 2
Tabulation of materials with and without adherent DLC coatings from each experiment (coatings that delaminated after exposure to air, are listed as *NOT* adherent)

Coating outcome	Experiment I	Experiment II	Experiment III
Adherent	M2, 4340, 1018, 303, Cr, Si, Al-A390	Mg, Al, Cr, 304, WC (Co), Si, M2, A36, Ti–6Al–4V, W	Mg, Al, Cr, 304, WC (Co), Si, M2, W, Ni, Ti–6Al–4V, brass
NOT adherent	Ti	Cu, brass, Ni	Cu, A36

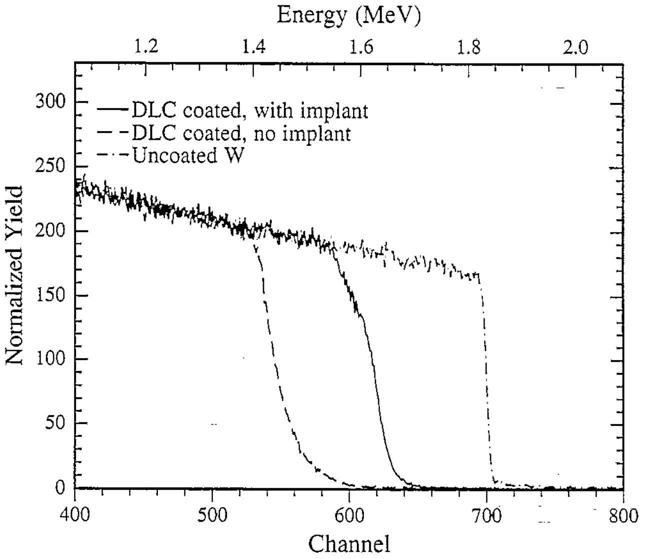

Fig. 1. RBS results for uncoated and DLC coated tungsten. The spectra show that carbon ion implantation, prior to DLC deposition, results in a interface graded in carbon composition. The presence of the graded interface is indicated by the reduced W yield in channels 595–620.

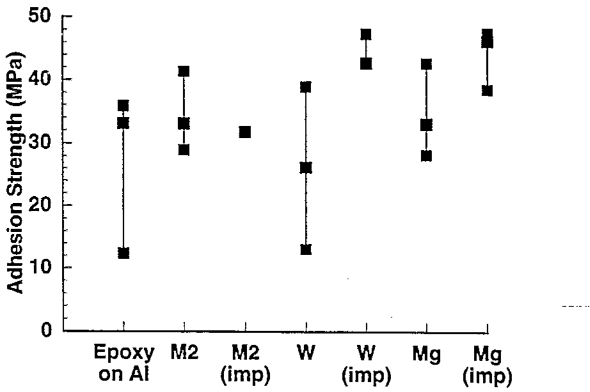

Fig. 2. Adhesion strengths of DLC coatings on M2 tool steel, W and Mg. Results from samples that included carbon implantation to strengthen the interface are labeled with "(imp)". The "Epoxy on Al" strength is included as an estimate of the strength of the epoxy.

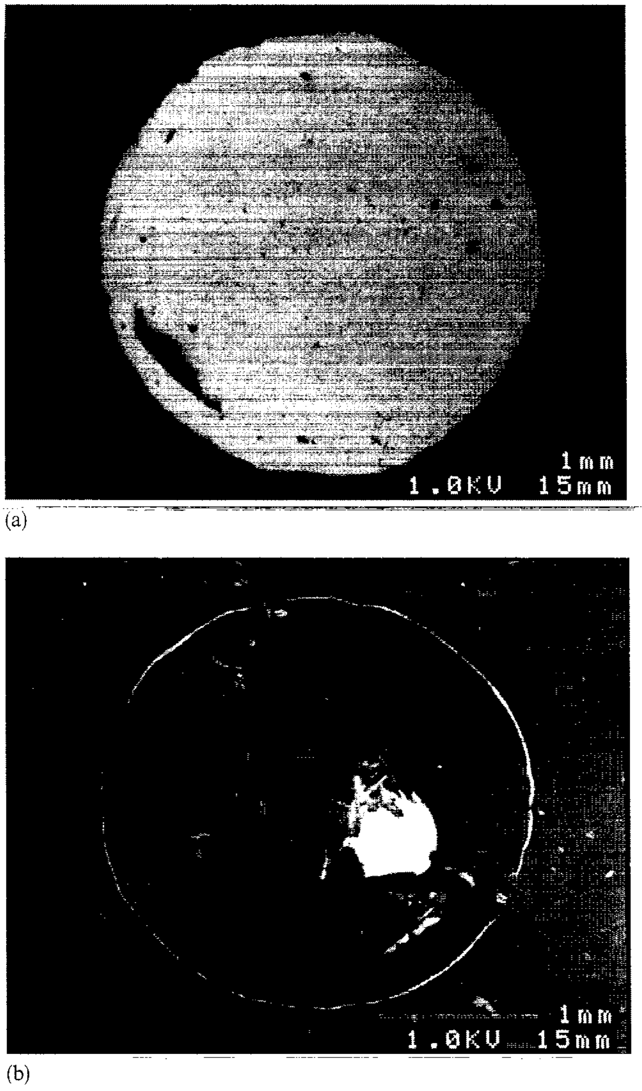

Fig. 3. SEM micrograph of DLC coated M2. (a) Without carbon implantation (Experiment II), the DLC coating is completely removed; (b) with carbon implantation (Experiment I), the DLC coating is more adherent and only partially removed. The tested area is ~2.8 mm in diameter.

in Figs. 3–5 which includes scanning electron microscopy (SEM) micrographs of the adhesion tested coatings. In all cases, the adhesion of the DLC coating improved as shown by the significant reduction in delaminated area for M2, and the complete absence of delaminated area for W and Mg. Considered together, the adhesion tests results and SEM micrographs show that enhanced DLC adhesion can be achieved by using ion implantation to create a graded interface between DLC and the metal. The SEM micrographs also confirm the epoxy generally forms the weakest interface for the adhesion test. Therefore, the reported adhesion strengths

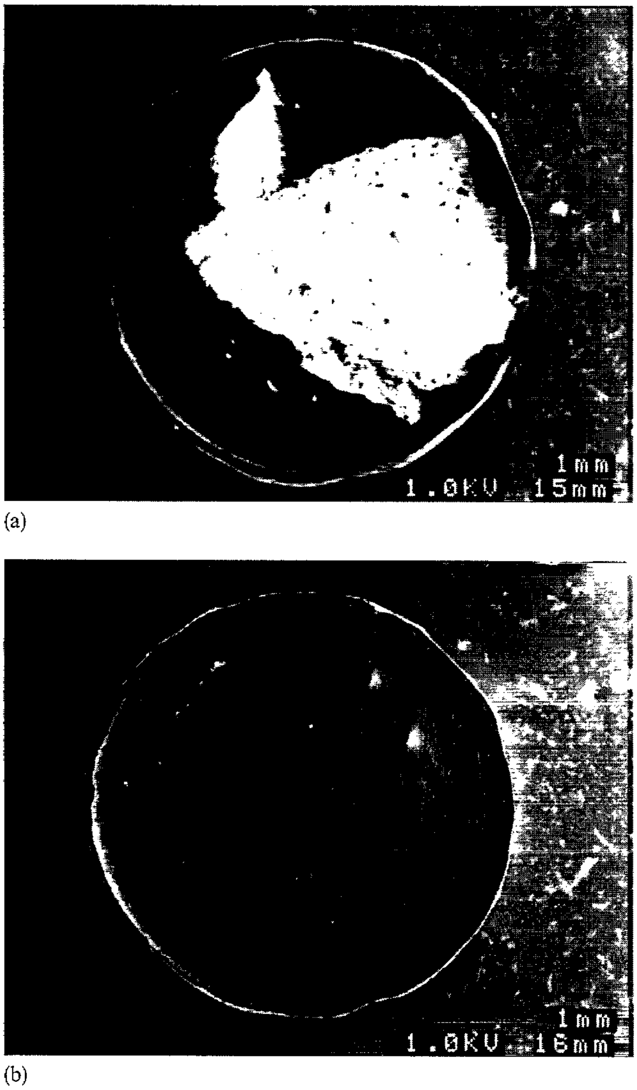

Fig. 4. SEM micrograph of DLC coated W. (a) Without carbon implantation (Experiment II), the DLC coating is partially removed; (b) with carbon implantation (Experiment III), the DLC coating is more adherent and no area of delamination is observed. The tested area is ~2.8 mm in diameter.

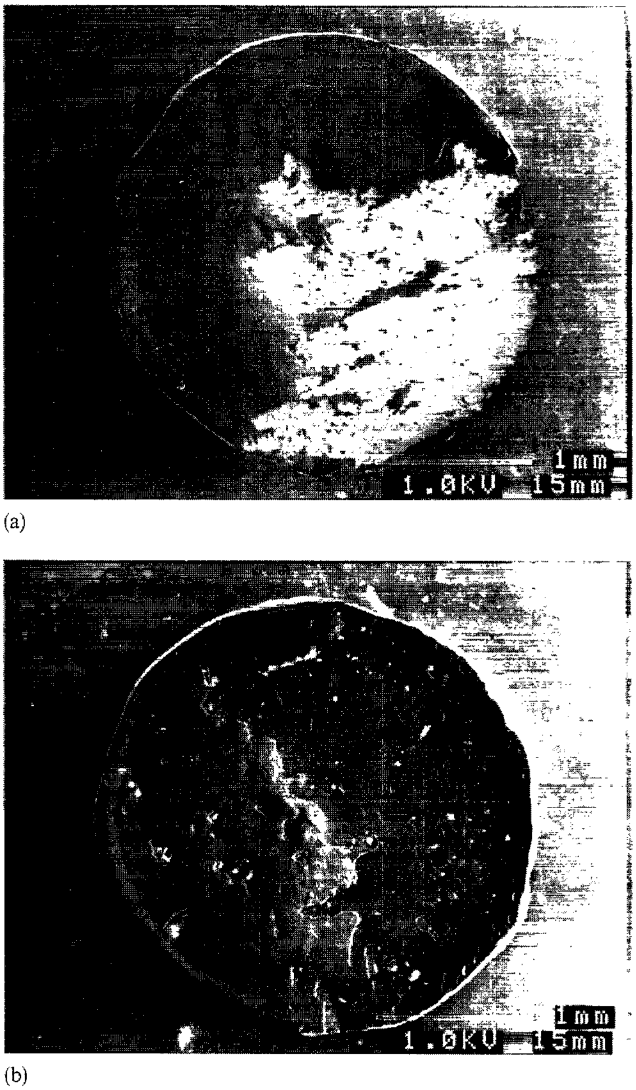

Fig. 5. SEM micrograph of DLC coated Mg (AM60). (a) Without carbon implantation (Experiment II), the DLC coating is partially removed; (b) with carbon implantation (Experiment III), the DLC coating is more adherent and no area of delamination is observed. The tested area is ~2.8 mm in diameter.

for the carbon implanted and DLC coated metals (Experiments I and III) can be viewed as a minimum estimate of the coating adhesion strength.

4. Conclusions

Carbon implantation using PSII can result in enhanced adherence of DLC coatings to metals. The enhanced adherence is due to graded interface, produced by carbon implantation, between the DLC coating and the metal substrate. DLC coatings can be deposited on metals with and without a thermodynamic driving force to form carbides because the carbon implantation process, on which coating adherence depends, is independent of thermodynamics. However, care must be taken to choose correct processing parameters for materials with thick oxides and proper cooling of components should not be neglected. This work shows that PSII can be used to produce adherent DLC coatings on a wide range of metals including Mg, Al, Si, Ti, Cr, Fe, Ni, Cu–Zn (brass) and W without the use of interlayers.

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